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Chemical reactions under ultra high pressure : reaction between urea and gypsum

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CHEMICAL REACTIONS UNDER ULTRA HIGH PRESSURE. REACTION BETWEEN UREA AND GYPSUM.

By RYO KIYAMA and TAKAO YANAGIMOTO.

Introduction.

When a mixed sample of urea and gypsum in solid state is placed in a certain relative humidity for several weeks at room temperature and atmospheric pressure, a urea-calcium sulphate complex is formed as shown in equation (1), which is already reported⁽¹⁾ by C. W. Whittaker, F. O. Lundstrom and S. B. Hendricks.



According to them, the rate of formation of the complex is very slow and greatly depends upon the degrees of relative humidity. Even in case of the relative humidity 67.5 % which gives the maximum yield, the yield of the complex is 11.04 % in a week and 91.19 % in 7 weeks, but in case of the relative humidity 50.4 % it is only 2.56 % in 7 weeks.

In the previous work⁽²⁾ it was expected that, when the pressure was applied to calcium sulphate dihydrate in solid state at room temperature, the crystal water might become unstable as a result of the shearing stress among all grains. Then, as it is to be expected that, if water is separated from the dihydrate by applying pressure, the solid reaction between dried urea and dried calcium sulphate dihydrate under high pressures will occur with the separated water and the crystal water replaced by urea, the present experiments have been carried out under the pressure range from 1 to 4,500 kg/cm² at room temperature and it is known that the reaction proceeds already in 30 minutes under a pressure of 3,000 kg/cm².

Experimentals.

(1) Samples.

Calcium sulphate used for the present experiment is the same with that used in the previous work⁽²⁾. Commercial urea is recrystallized from its aqueous solution and dried up perfectly in a desiccator with CaCl₂.

(2) Apparatus and procedure.

The high pressure apparatus has already been reported⁽³⁾. Mixing dried urea with calcium sulphate in an agate mortar at the ratio of 4 mols to 1 is subjected to any desired pressure for desired time in the pressure vessel.

(3) Analytical method.

(1) C. W. Whittaker, F. O. Lundstrom and S. B. Hendricks, *Ind. Eng. Chem.*, **25**, 1280 (1933)

(2) R. Kiyama and T. Yanagimoto, *This Journal*, **22**, 34 (1952)

(3) R. Kiyama and T. Yanagimoto, *This Journal*, **21**, 32 (1951)

After the pressure has been released, the sample is smashed thoroughly and the unreacted urea is isolated by washing with anhydrous methyl alcohol. The precipitate thus obtained is dried up in an air-bath at 60°C until the odour of alcohol disappears and the amount of conversion to urea-calcium sulphate complex is determined from the measurement of the total nitrogen by the Kjeldahl method.

Experimental Results.

(1) Reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CO}(\text{NH}_2)_2$.

These results are given in Table 1. At atmospheric pressure the complex can not be formed in the air when the mixed sample is placed as it is for 2 hours. When a pressure of 1,500 kg/cm² is applied, the sample is hardened and becomes semitransparent, but the yield of the complex is very small in amount even in 2 hours. On the other hand, under a pressure of 3,000 kg/cm², the dehydration occurs and the pressure effect becomes remarkable. Then, the pressure-applied sample is not hardened and, moreover, the separation of water is observed. Applying a pressure of 4,500 kg/cm² for 60 minutes, it seems that the reaction reaches an equilibrium.

Table 1
The yield of urea-calcium sulphate complex (%).
Temperature: 25°C

| Pressure (kg/cm ²) | Durations of the pressure applied (min.). | | | | |
|--------------------------------|---|------|------|------|------|
| | 0 | 10 | 30 | 60 | 120 |
| 1 | | | | | 0.0 |
| 500 | | | | | 0.19 |
| 1,500 | 0.18 | | 0.20 | 0.23 | 0.26 |
| 3,000 | 0.23 | 1.40 | 4.43 | 5.58 | 7.28 |
| 4,500 | 0.28 | 1.60 | 6.43 | 7.62 | 7.41 |

(2) Reactions of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 4\text{CO}(\text{NH}_2)_2$.

In the use of hemihydrate in place of the dihydrate, the yield of the complex is very small in amount, even if a pressure of 4,500 kg/cm² is applied for 30 minutes. And the hardening of the pressure-applied samples is observed.

Table 2
The yield of urea-calcium sulphate complex (%).
Temperature: 25°C, Pressure: 4,500 kg/cm².

| Reaction systems | Durations of the pressure applied (min.). | | |
|---|---|------|------|
| | 0 | 10 | 30 |
| $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 4\text{CO}(\text{NH}_2)_2$ | 0.16 | 0.14 | 0.67 |
| $\text{CaSO}_4(\text{soluble}) + 4\text{CO}(\text{NH}_2)_2$ | | | 0.35 |
| $\text{CaSO}_4(\text{insoluble}) + 4\text{CO}(\text{NH}_2)_2$ | | | 0.0 |

(3) Reaction of $\text{CaSO}_4(\text{soluble}) + 4\text{CO}(\text{NH}_2)_2$.

The formation of a small amount of the complex in this reaction may be ascribed to the absorption of some water by soluble anhydride during the operation.

(4) Reaction of $\text{CaSO}_4(\text{insoluble}) + 4\text{CO}(\text{NH}_2)_2$.

This reaction does not occur entirely even if a pressure of $4,500 \text{ kg/cm}^2$ is applied for 30 minutes.

(5) Influence of water on the reaction of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CO}(\text{NH}_2)_2$.

Table 3

The yield of urea-calcium sulphate complex from the reactions of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 4\text{CO}(\text{NH}_2)_2 + x\text{H}_2\text{O}$.

Temperature: 25°C , Pressure: 500 kg/cm^2 ,
Duration of the Pressure applied: 30 min..

| x (mols) | Yield (%) |
|----------|-----------|
| 0 | 0.14 |
| 0.5 | 0.20 |
| 1.0 | 7.68 |
| 1.5 | 8.15 |

In case of adding 1 mol of water to this system, the yield of the complex is only 0.24 % under atmospheric pressure in 30 minutes, but it increases to 7.68 % under 500 kg/cm^2 in the same minutes.

As for changing a quantity of the added water, the reaction is scarcely accelerated by adding 0.5 mols of water, but the effect of 1 mol of water is more distinct as shown in Table 3.

Considerations.

At room temperature and atmospheric pressure, W. Sakai already pointed out⁽⁴⁾ that a definite quantity of water was always required for the solid reaction as a promoting agent.

On the other hand, seeing from the experimental results that the presence of a definite quantity of water accelerates the reaction under 500 kg/cm^2 and the absence of it scarcely even under $1,500 \text{ kg/cm}^2$, the high pressure solid reaction will need a definite quantity of water as well as at atmospheric pressure. In case of experimental results (1) the water does not exist, but the reaction is promoted under $3,000 \text{ kg/cm}^2$. It seems because that a definite quantity of water from the dihydrate is separated by shearing stress among crystal grains when the compression is increased up to the pressure. But, under pressures below $1,500 \text{ kg/cm}^2$, it seems because that the dehydration of dihydrate is imperfect and as a definite quantity of water can not be formed the reaction is not accelerated.

Further, a pressure of $4,500 \text{ kg/cm}^2$ is applied to the mixed samples of urea and either anhydride or hemihydrate, but the complex is scarcely formed, as shown in Table 2. This reason is also considered as follows: because of lacking or nothing of the water which may be isolated by compression, a definite quantity of water can not be formed distinctly.

This consideration is in agreement with the experimental results in the previous

(4) W. Sakai, *J. Soc. Chem. Ind. Japan*, 43, 716 (1940)

work⁽²⁾ on the dehydration of calcium sulphate dihydrate under high pressure which have been expected from the difference of dehydration curves between the reactions under 5,000 kg/cm² and 500 kg/cm². Then, this experimental result supports the expectation of the dehydration of the dihydrate by applying pressure.

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